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<b>(21) International Application Number:</b> PCT/US99/08191 <b>(22) International Filing Date:</b> 14 April 1999 (14.04.99) <b>(30) Priority Data:</b> 09/063,472 20 April 1998 (20.04.98) US <b>(71) Applicant:</b> PPG INDUSTRIES OHIO, INC. [US/US]; 3800 West 143rd Street, Cleveland, OH 44411 (US). <b>(72) Inventors:</b> McCOLLUM, Gregory, J.; 5130 Bronwyn Court, Gibsonia, PA 15044 (US). O'DWYER, James, B.; 111 Spring Valley Road, Valencia, PA 16059 (US). COCA, Simion; Apartment 28, 4 Bayard Road, Pittsburgh, PA 15213 (US). <b>(74) Agents:</b> UHL, William, J.; PPG Industries, Inc., One PPG Place, Pittsburgh, PA 15272 (US) et al.		<b>(81) Designated States:</b> AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> REMOVAL OF HALOGENS FROM POLYMERIZATION PRODUCT AND THE REDUCED HALOGEN POLYMER AND METHOD  <b>(57) Abstract</b>  A controlled free radical polymer of the living variety from atom transfer radical polymerization (ATRP) with a reduced halogen content and method are provided. The ATRP polymer is prepared from ATRP reactable monomers in the presence of one or more transition metals and stabilizing ligands and initiators. The resulting ATRP polymer is further reacted with a limited polymerizable double bond containing compound (LPDB compound). The LPDB compound allows for an addition reaction with the ATRP polymer at the halogen containing terminal portion of the polymer along with the elimination of the halogen from the ATRP polymer.		

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## REMOVAL OF HALOGENS FROM POLYMERIZATION PRODUCT AND THE REDUCED HALOGEN POLYMER AND METHOD

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The present invention is directed to a process for removing halogens from the ends or terminal locations of polymers and the resulting reduced halogen-containing polymers. The halogen-containing polymers are typically produced from living polymerization processes utilizing halogen-containing compounds.

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"Living polymerization" refers to a polymerization where there is essentially no chain transfer and essentially no chain termination reactions, and usually includes types of polymerizations such as: anionic, cationic, and covalent. These living polymerizations involve limited, if any, reaction of the chain ends with each other so that monomers add to the growing polymer chain one at a time. To varying

15 degrees these polymerizations produce polymers with structured architecture and with very narrow molecular weight distribution. Types of polymer architecture that are possible from one or more of these polymerizations, although possibly not from each, include: graft; comb-shaped; multiple-legged, like star-shaped; ladder-shaped; cyclic and blocked copolymers like AB and ABA structures. In these

20 polymerizations the active ends of the growing polymer chain may terminate in reactions with impurities or intentionally added terminating groups. For instance, several such polymerization processes for producing living polymers have halogen materials as part of the initiator, a reactant, ligand, and/or metal catalyst used in the polymerization that may become part of the terminating group of the polymer.

25

A recent polymerization system utilizing a free radical or group transfer approach also results in polymers of controlled architecture and narrow molecular weight distributions and can be considered living polymerization. Such polymerizations are disclosed in the following World Patent Publications of PCT applications WO96/30421, WO97/1824 and WO98/01480. These applications

30 disclose the controlled free radical production of polymers based on an atom transfer process based on a redox reaction with a transition metal compound. This process involves polymerizing one or more radically polymerizable monomers in the

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presence of an initiating system which has an initiator with a radically transferable atom or group, a transition metal compound which participates in a reversible redox cycle, for example with the initiator, and a ligand. The ligand can have any nitrogen, oxygen, phosphorous, sulfur-containing compound, or any carbon-  
5 containing compound which can coordinate with the transition metal. Organic halides can function as halogen atom transfer precursors or initiators in the process as well as transition metal complexes as halogen atom transfer promoters. So halogen-containing polymers result from the atom or group transfer polymerization process where a halogen-containing compound generally reacts with ethylenically  
10 unsaturated monomers in a living polymerization manner. This atom or group transfer polymerization process has been referred to as Atom Transfer Radical Polymerization (hereinafter referred to as "ATRP").

Some of the advantages of low polydispersity index and tailor-made arrangement of polymer architecture or structure or topology for living  
15 polymerizations may not be fully utilized in some applications because of the presence of halogens. The polymers having halogens as a result of the polymerization process and chemical formulations or compositions with such polymers can lead to corrosion of handling equipment or difficulty in disposal of waste streams with such polymers. For instance, where the polymers are used in  
20 formulations or compositions handled by metallic devices, such as pumps, tubing, containers, or spraying apparatus, the halogens would cause a corrosion problem with such devices. This is more of a problem with the lower molecular weight polymers since the concentration of the halogen is higher for the lower molecular weight polymers compared to the higher molecular weight polymers. For sprayable  
25 compositions such as those with polymers in the lower molecular weight range of less than 100,000, weight average molecular weight ("Mw"), and with appropriate viscosities, the presence of the halogen-containing living polymers would result in corrosion problems with the spraying equipment. Also for adhesives containing

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these halogen-containing living polymers, the durability of the adhesive bond to metals would be an issue. Additionally, where the polymers are used as lubricants or lubricant modifying compositions, the use may be impeded by such corrosion concerns. Also cleanup by combustion of the used lubricants having some halogen  
5 concentration may generate acid of hydrohalogen compounds like hydrochloric acid.

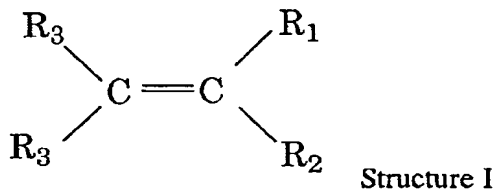
One method of reducing the chlorine content of various organochlorine compounds is disclosed in U.S. Patent 5,708,097. An organo compound such as chlorine containing mixtures of polyalkene-substituted succinic anhydride and chlorine which maybe free and/or bonded chlorine such as polyalkenylchloride,  
10 chlorinated polyalkenylsuccinic anhydride, chlorinated succinic anhydride polyalkenylsuccinic anhydride is contacted with a source of iodine or bromine for a sufficient time to reduce the chlorine content. The resultant mixture is contacted with a polyamine. Such a process involves a two-step reaction process, wherein the introduction of other halogens such as bromine or iodine which, if not removed,  
15 would still leave halogen compounds present.

It is an object of the present invention to reduce the halogen content of living polymers, like those from ATRP, produced with halogen-containing components that result in the incorporation of the halogen into the polymer in a facile process resulting in polymeric materials with non-halogen containing end groups. A further  
20 object of the present invention is to produce polymers with reduced halogen content from living polymerization processes, like ATRP, under mild conditions while minimizing the production of any additional waste streams. The use of such polymers with reduced halogen content lessens any corrosivity to handling equipment for the polymer and for formulations and compositions containing the  
25 polymer.

A further object of the invention is to produce polymers with reduced halogen contents to avoid production of hydrogen halogen compounds like hydrogen chloride gas in combustion gases during incineration of waste polymeric materials.

### SUMMARY OF THE INVENTION

The aforementioned objects of the invention are realized as well as other objects gleaned from the following disclosure by the process and composition of the present invention. The present invention involves reacting halogen-containing living-type polymers with one or more compounds having an unsaturated double-bond and not readily polymerizable with itself under ATRP reaction conditions. The halogen-containing polymers are typically produced from polymerization processes such as ATRP polymerization utilizing halogen-containing reactants, initiators and/or catalysts. The halogen-containing polymer reacts with the limited polymerizable double-bond containing compound through addition at the double-bond and the resulting reaction product or intermediate allows for an elimination reaction of the halogen from the polymer. Suitable limited polymerizable double-bond containing compounds include organo-substituted ethylenic or olefinic unsaturated compounds such as those having the structure:



In this structure  $R_1$  and  $R_2$  can be the same or different organic groups such as: alkyl groups having a number of carbon atoms from 1 to 4; aryl groups; alkoxy groups; ester groups; alkyl sulfur groups, acyloxy groups, nitrogen-containing alkyl groups where at least one of the  $R_1$  and  $R_2$  groups is an organo group while the other can be an organo group or hydrogen. For instance when one of  $R_1$  or  $R_2$  is an alkyl group, the other can be an alkyl, aryl, acyloxy, alkoxy, arenes, sulfur-containing alkyl group, or nitrogen-containing alkyl and/or nitrogen-containing aryl groups. The  $R_3$  groups can be the same or different groups selected from hydrogen or lower alkyl selected such that the addition reaction of the halogen-containing

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polymer to the double-bond is not prevented. Also an  $R_3$  group can be joined to the  $R_1$  and/or the  $R_2$  groups to form a cyclic compound. Generally, the reaction conditions for the addition reaction of the limited polymerizable double-bond containing compound with the halogen containing polymer involves the presence of  
5 catalyst for ATRP-type polymerization to effect the reaction, and the maintenance of the temperature and time sufficient to cause the desired reaction to occur.

Alternatively, the addition and elimination reactions can be conducted at different temperatures; for instance, the addition at a low temperature and the elimination by gentle heating of the addition product.

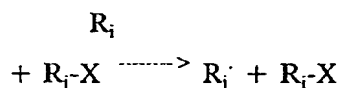
10 The controlled free radical polymerized living polymer that contains halogen can be in the form of a solution or liquid which is already in contact with the catalyst and/or initiator from the ATRP polymerization process. To such a system the addition of the limited polymerizable double-bond compound along with the maintenance of ATRP reaction conditions produces the non-halogen containing  
15 polymer. Alternatively, the living polymer containing the halogen can be one that has been isolated from the polymerization materials or system. To this type of system, the limited polymerizable double bond containing compound along with other reaction materials like those found in the aforementioned ATRP system are added. In this latter reaction an initiator need not be added, but, of course, the  
20 initiator could still be added. Any solvent that does not interfere with the polymerization process can be used.

A suitable halogen containing living polymer is that where the term "living" or "controlled" refers to polymerization where chain breaking reactions such as transfer and termination are minimized or preferably substantially absent. Such  
25 polymerization enables control of various parameters of macromolecular structure such as molecular weight, molecular weight distribution and terminal functionalities. It also allows the preparation of various copolymers, such as one or more of block, graft, multi-legged, and star copolymers. Such polymerizations can be considered

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as based on a univalent atom (typically a halogen) that is transferred from a neutral molecule to a radical to form a new bond and a new radical in accordance with Scheme 1 below:

5 Scheme 1:



X = is halogen like chlorine, bromine, or iodine, and the like.

For these reactions it has been indicated that a catalytic amount of transition  
 10 metal compound can act as a type of carrier of the halogen atom in a redox process. Initially, the transition metal species,  $M_i^n$ , abstracts halogen atom X from the organic halide,  $R_j-X$ , to form the oxidized species, such as  $M_i^{n+1}X$ , and the carbon-centered radical such as  $R_j\cdot$ . In the subsequent step, the radical,  $R_j\cdot$ , can react with alkene, monomer ("M"), with the formation of the intermediate radical species,  $R_j-M\cdot$ .  
 15  $M\cdot$ . The reaction between  $M_i^{n+1}X$  and  $R_j-M\cdot$  results in the target product,  $R_j-M-X$ , and regenerates the reduced transition metal species,  $M_i^n$ , which further reacts with  $R-X$  and promotes a new redox process. A suitable process for such polymerization is that referred to as atom (or group) transfer radical polymerization or "ATRP".

The description of the ATRP process for ATRP conditions comprises: polymerizing  
 20 one or more radically polymerizable monomers in the presence of an initiator having a radically transferable atom or group, a transition metal compound and a ligand to form a polymer or copolymer, hereinafter "(co)polymer", where direct (i.e., covalent) bonds between the transition metal and growing polymer radicals are limited or minimized and preferably not formed. The resulting polymer may or may  
 25 not be isolated. The organic halide  $R_j-M_i-X$  resulting from atom transfer radical addition reaction is sufficiently reactive towards the transition metal  $M_i^n$ , and the alkene monomer is in excess so that a number or sequence of atom transfer radical additions (i.e., a possible "living"/controlled radical polymerization) occurs.

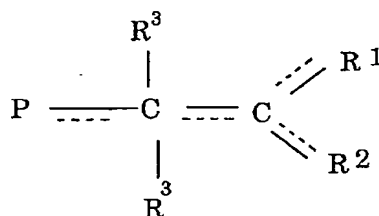


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With the addition and elimination reaction resulting from the limited polymerizable double-bond compound, the polymer has a non-halogen end group or terminal groups as depicted in Structure II below:

5

Structure II



In Structure II "P" indicates the polymer chain portion of an ATRP halogen-containing (co)polymer without the group of the ATRP that contains the halogen. The latter group is that derived from the last "living" monomer to add to the (co)polymer. Also in Structure II, the  $R_3$ , C,  $R_1$  and  $R_2$ - portion of the polymer is one of the one or more non-halogen end or terminal groups of the polymer of the present invention. In Structure II,  $R_1$ ,  $R_2$ , and  $R_3$ , can be groups as discussed for Structure I above. In Structure II the dotted lines accompanying the bonds indicate that any one of those bonds can be a double bond or an unsaturated bond, and where one of the dashed lines becomes the double bond, the other dashed lines essentially revert to the single bonds. In the event that the non-halogenated end group of the polymer can tautomerize, for example, from an enol group to a ketone group, these structures are also meant to be included in Structure II.

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#### DETAILED DESCRIPTION OF THE INVENTION

Suitable living or controlled free radically produced polymers can be obtained from the ATRP process as described in the World Patent Publications of

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PCT applications WO96/30421, WO97/01824, and WO98/01480, all of which are hereby incorporated in their entirety by reference.

In the aforelisted PCT publications, such ATRP polymerization involves the initiating systems based on the reversible formation of growing radicals in a redox  
5 reaction between various transition metal compounds and an initiator, nonlimiting examples of which are: alkyl halides, aralkyl halides or haloalkyl esters. For instance, 1-phenylethyl chloride (1-PECl) can be the initiator where CuCl is the catalyst and bipyridine (Bpy) is a stabilizing ligand in producing a "living" radical bulk polymerization of styrene at 130°C. A narrow molecular weight distribution  
10 (e.g.,  $M_w/M_n < 1.5$ ) is reported where the predicted number average molecular weight ("Mn") is up to  $M_n \gg 10^5$ . In such polymerizations note has been made of achieving a rapid exchange between growing radicals present at low stationary concentrations (in the range of from  $10^{-9}$  mol/L to  $10^{-6}$  mol/L, preferably  $10^{-8}$  mol/L to  $10^{-6}$  mol/L) and dormant chains present at higher concentrations (typically in the  
15 range  $10^{-4}$  mol/L to 1 mol/L, preferably  $10^{-2}$  mol/L to  $10^{-1}$  mol/L). It is possible in the ATRP process to achieve such concentration ranges by matching the concentrations and/or types of initiator/catalyst/ligand system and monomer(s). As in the above-referenced patent documents for the ATRP polymerization, the following terms have the indicated meaning.

20 The terms "Alkyl", "alkenyl" and "alkynyl" refer to straight-chain or branched groups (except for  $C^1$  and  $C^2$  groups).

The term "Aryl" refers to phenyl, naphthyl, phenanthryl, phenalenyl, anthracenyl, triphenylenyl, fluoranthenyl, pyrenyl, pentacenyl, chrysenyl, naphthacenyl, hexaphenyl, picenyl and perylenyl (preferably phenyl and naphthyl),  
25 in which each hydrogen atom may be replaced with alkyl of from 1 to 20 carbon atoms (preferably from 1 to 6 carbon atoms and more preferably methyl), alkyl of from 1 to 20 carbon atoms (preferably from 1 to 6 carbon atoms and more preferably methyl) in which each of the hydrogen atoms is independently replaced

by a halide (preferably a fluoride or a chloride), alkenyl of from 2 to 20 carbon atoms, alkynyl of from 1 to 20 carbon atoms, alkoxy of from 1 to 6 carbon atoms, alkylthio of from 1 to 6 carbon atoms, C<sub>3</sub>-C<sub>8</sub> cycloalkyl, phenyl, halogen, NH<sub>2</sub>, C<sub>1</sub>-C<sub>6</sub>-alkylamino, C<sub>1</sub>-C<sub>6</sub>-dialkylamino, and phenyl which may be substituted with from  
5 1 to 5 halogen atoms and/or C<sub>1</sub>-C<sub>4</sub> alkyl groups. (This definition of "aryl" also applies to the aryl groups in "aryloxy" and "aralkyl"). Thus, phenyl may be substituted from 1 to 5 times and naphthyl may be substituted from 1 to 7 times (preferably, any aryl group, if substituted, is substituted from 1 to 3 times) with one of the above substituents. More preferably, "aryl" refers to phenyl, naphthyl,  
10 phenyl substituted from 1 to 5 times with fluorine or chlorine, and phenyl substituted from 1 to 3 times with a substituent selected from the group consisting of alkyl of from 1 to 6 carbon atoms, alkoxy of from 1 to 4 carbon atoms and phenyl. Most preferably, "aryl" refers to phenyl, tolyl and methoxyphenyl.

The term "heterocyclyl" refers to such compounds as: pyridyl, furyl,  
15 pyrrolyl, thienyl, imidazolyl, pyrazolyl, pyrazinyl, pyrimidinyl, pyridazinyl, pyranyl, indolyl, isoindolyl, indazolyl, benzofuryl, isobenzofuryl, benzothienyl, isobenzothienyl, chromenyl, xanthenyl, purinyl, pteridinyl, quinolyl, isoquinolyl, phthalazinyl, quinazolinyl, quinoxalinyl, naphthyridinyl, phenoxathiinyl, carbazolyl, cinnolinyl, phenanthridinyl, acridinyl, 1,10-phenanthrolinyl, phenazinyl,  
20 phenoxazinyl, phenothiazinyl, oxazolyl, thiazolyl, isoxazolyl, isothiazolyl, and hydrogenated forms thereof known to those in the art.

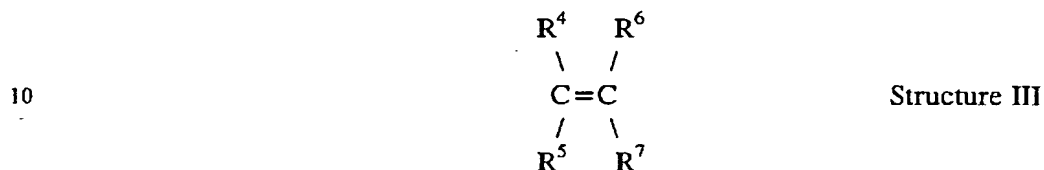
The term "controlled" refers to the ability to produce a product having one or more properties which are reasonably close to their predicted value (presuming a particular initiator efficiency). For example, if one assumes 100% initiator efficiency,  
25 the molar ratio of catalyst to monomer leads to a particular predicted molecular weight. The polymerization is said to be "controlled" if the resulting number average molecular weight is reasonably close to the predicted number average molecular

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weight, e.g., within an order of magnitude, preferably within a factor of four, more preferably within a factor of three and most preferably within a factor of two.

### MONOMERS FOR ATRP

5 As described in the aforelisted PCT publications for ATRP polymerization, any radically polymerizable alkene generally can serve as a (M) monomer with ethylenic unsaturation for polymerization such as those of the formula or structure:



The  $R^4$  and  $R^5$  can be selected independently from the group consisting of: 1) hydrogen, halogen, CN,  $CF_3$ , straight or branched alkyl of from generally 1 to 20 carbon; 2) alpha ( $\alpha$ ), beta ( $\beta$ )-unsaturated straight or branched alkenyl or alkynyl of 2 to 10 carbon; 3) halogen substituted  $\alpha,\beta$ -unsaturated straight or branched alkenyl of 2 to 6 carbon atoms; 4)  $C_3$ - $C_8$  cycloalkyl; 5) heterocyclyl; and 6) a group such as  $C(=Y)R^8$ ,  $C(=Y)NR^9R^{10}$  and  $YC(=Y)R^{11}$ ,  $YC(=Y)R^8$ ,  $SOR^8$ ,  $SO_2R^8$ ,  $OSO_2R^8$ ,  $NR^{11}SO_2R^8$ ,  $PR^8_2$ ,  $P(=Y)R^8_2$ ,  $YPR^8_2$ ,  $YP(=Y)R^8_2$ ,  $YC(=Y)R^{11}$ ,  $YC(=Y)YR^{11}$ ,  $YS(=Y)^{11}$ ,  $YS(=Y)_2R^{11}$ ,  $YS(=Y)_2YR^{11}$ ,  $P(R^{11})_2$ ,  $P(=Y)(R^{11})_2$ ,  $P(YR^{11})_2$ ,  $P(=Y)(YR^{11})_2$ ,  $P(YR^{11})R^{11}$ ,  $P(=Y)(YR^{11})R^{11}$ ,  $NR^{11}_2$  which may be quaternized with an additional  $R^{11}$  group ( $N^+R^{11}_3$ ), aryl and heterocyclyl. The alkyl group in group (1) above and the alkenyl or alkynyl groups of group (2) above and the cycloalkyl of group (3) above may be substituted with from 1 to  $(2n+1)$  halogen atoms where n is the number of carbon atoms of the alkyl group (e.g.  $CH_2=CCl-$ ). In group (6) above Y may be  $NR^{11}$  S or O (preferably O);  $R^8$  is alkyl of from 1 to 20 carbon atoms, alkylthio of from 1 to 20 carbon atoms,  $OR^*$  (where  $R^*$  is H or an alkali metal), alkoxy of from 1 to 20 carbon atoms, aryloxy or heterocyclyloxy;  $R^9$  and  $R^{10}$  are independently hydrogen or alkyl of from 1 to 20 carbon atoms, or  $R^9$  and  $R^{10}$  may

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be joined together to form an alkylene group of from 2 to 5 carbon atoms, thus forming a 3- to 6-membered ring. Further in (6),  $R^{11}$  can be hydrogen, straight or branched  $C_1$ - $C_{20}$  alkyl or aryl groups, which may be joined to form a 3- to 8-membered ring where more than one  $R^{11}$  group is covalently bound to the same atom, or aryl, and when  $R^{11}$  is directly bonded to S or O, it may be an alkali metal or an ammonium ( $N^+R_4^8$ ) group. Also for group (1) above, a particularly suitable number of carbon atoms for the groups is from 1 to 6 while a more suitable number is from 1 to 4. For the group (2) above, a particularly suitable number of carbon atoms is 2 to 6 and more suitably 2 to 4 carbon atoms. For group (3) above, a particularly suitable halogen is chlorine which is at the  $\alpha$  position and a suitable unsaturation is vinyl.

$R^6$  and  $R^7$  of Structure III may be independently selected from the group consisting of: hydrogen, halogen (preferably chlorine),  $C_1$ - $C_6$  (preferably  $C_1$ ) alkyl and  $COOR^{**}$ , where  $R^{**}$  is hydrogen, an alkali metal, or a  $C_1$ - $C_6$  alkyl group.

Also  $R_4$  and  $R_6$  may be joined to form a group of the formula  $(CH_2)_n$ , and this group can be substituted with from 1 to  $2n$  halogen atoms or  $C_1$ - $C_4$  alkyl groups or  $C(=O)$ -Y- $C(=O)$ , where  $n$  is from 2 to 6 (preferably 3 or 4) and Y is as defined above. Also in Structure III above, at least one of  $R^4$ ,  $R^5$ ,  $R^6$  and  $R^7$  is halogen and at least two of  $R^4$ ,  $R^5$ ,  $R^6$  and  $R^7$  are hydrogen or halogen.

Additionally, any radically polymerizable alkene of Structure III containing a polar group like the nitrile (CN) group can serve as a monomer for polymerization. For instance  $R_7$  of Structure III can be a polar group like the CN group.

Nonexclusive illustrative examples of several types of the aforementioned monomers include: 1') (meth)acrylate esters of  $C_1$ - $C_{20}$  alcohols, 2') acrylonitrile, 3')

cyanoacrylate esters of  $C_1$ - $C_{20}$  alcohols, 4') dihydromalonate diesters of  $C_1$ - $C_6$  alcohols, 5') vinyl pyridines, 6') vinyl N- $C_1$ - $C_6$ -alkylpyrroles, 7') vinyl oxazoles, 8') vinyl thiazoles, 9') vinyl pyrimidines and vinyl imidazoles, 10') certain types of vinyl ketones, and 11') styrene. For the vinyl ketones of (10') above, the  $\alpha$ -carbon

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atom of the alkyl group does not have a hydrogen atom. Examples include: vinyl C<sub>1</sub>-C<sub>6</sub>-alkyl ketones in which both  $\alpha$ -hydrogens are replaced with C<sub>1</sub>-C<sub>4</sub> alkyl and/or halogen and the like, or a vinyl phenyl ketone in which the phenyl may be substituted with from 1 to 5 substituents that are C<sub>1</sub>-C<sub>6</sub>-alkyl groups and/or halogen atoms. The styrenes can have a C<sub>1</sub>-C<sub>6</sub>-alkyl group on the vinyl group, preferably at the  $\alpha$ -carbon atom, and from 1 to 5, preferably from 1 to 3, substituents on the phenyl ring selected from the group consisting of C<sub>1</sub>-C<sub>6</sub>-alkyl, C<sub>1</sub>-C<sub>6</sub>-alkenyl (preferably vinyl), C<sub>1</sub>-C<sub>6</sub>-alkynyl (preferably acetylenyl), C<sub>1</sub>-C<sub>6</sub>-alkoxy, halogen, nitro, carboxy, C<sub>1</sub>-C<sub>6</sub>-alkoxycarbonyl, hydroxy protected with a C<sub>1</sub>-C<sub>6</sub> acyl, cyano and phenyl. As noted in the aforementioned world patent documents, the most suitable monomers are methyl acrylate (MA), methyl methacrylate (MMA), butyl acrylate (BA), 2-ethylhexyl acrylate (EHA), acrylonitrile (AN) and styrene. Also any other monomers disclosed in WO96/30421 and/or WO97/1824 and/or WO98/01480 can be used. The aforementioned monomers result in the (co)polymer with a halogen in the terminal or end portion of the polymer chain since these types of monomers do not readily lose halogen from the formed (co)polymer.

Also monomers can be used with functional groups or with precursor groups of functional groups. For example, the end functionality of the (co)polymers produced by the ATRP process (e.g., Cl, Br, I, ON, CO<sub>2</sub>R) can be a precursor group that easily is converted to other functional groups. For example, groups such as Cl, Br and I can be converted to OH or NH<sub>2</sub> by known processes, and CN or CO<sub>2</sub>R can be hydrolyzed to form a carboxylic acid by known processes, and a carboxylic acid may be converted by known processes to a carboxylic acid halide. The presence of these functional groups could facilitate chain extension processes as in the formation of long-chain polyamides, polyurethanes and/or polyesters. Also in some cases, as where "X" is Cl, Br and I, the end functionality of the (co)polymers produced by the ATRP process can be reduced by known methods to provide end groups having the same structure as the repeating polymer units.

An initiator system for ATRP has been described as having an initiator, transition metal compound, and ligand as further described below.

#### INITIATOR FOR ATRP

5        Suitable initiators reported for the ATRP process include those of the formula:



where:

X is selected from the group consisting of Cl, Br, I,  $OR^{16}$ ,  $SR^{17}$ ,  $SeR^{17}$ ,  
 10     $OC(=O)R^{17}$ ,  $OP(=O)R^{17}$ ,  $OP(=O)(OR^{17})_2$ ,  $OP(=O)OR^{17}$ ,  $O-N(R^{17})_2$  and  
 $S-C(=S)N(R^{17})_2$ . The  $R^{16}$  group is an alkyl of from 1 to 20 carbon atoms, in which  
 each of the hydrogen atoms may be independently replaced by groups such as  
 halide, alkenyl, alkynyl, phenyl or substituted phenyl with 1 to 5 halogen atoms or  
 alkyl groups of 1 to 4 carbon atoms, or aralkyl groups. The  $R^{17}$  is aryl or a straight  
 15    or branched  $C_1$ - $C_{20}$ , preferably  $C_1$ - $C_{10}$ , alkyl group, or where an  $N(R^{17})_2$  group is  
 present. Also the two  $R^{17}$  groups may be joined to form a 5-, 6- or 7-membered  
 heterocyclic ring (in accordance with the definition of "heterocyclyl" above).  
 The  $R^{13}$ ,  $R^{14}$  and  $R^{15}$  groups are each independently selected from the group  
 consisting of: groups like those for  $R^4$  and  $R^5$  of Structure III at (1), and (4), above  
 20    (other than the  $CF_3$ ), and  $C(=Y)R^8$ ,  $C(=Y)NR^9R^{10}$  of (6) above,  $COCl$ ,  $OH$ ,  
 although where most suitably only one of  $R^{13}$ ,  $R^{14}$  and  $R^{15}$  is  $OH$ ,  $C_2$ - $C_{20}$  alkenyl or  
 alkynyl, where more suitably  $C_2$ - $C_6$  alkenyl or alkynyl, and even more suitably  
 vinyl; oxiranyl, glycidyl, aryl, heterocyclyl, aralkyl, aralkenyl, aryl-substituted  
 alkenyl, and alkenyl is vinyl which may be substituted with one or two  $C_1$ - $C_6$  alkyl  
 25    groups and/or halogen atoms, like chlorine; and  $C_1$ - $C_6$  alkyl. In the latter alkyl  
 group from 1 to all of the hydrogen atoms are replaced with halogen, suitably  
 fluorine, chlorine or bromine and where most suitably 1 hydrogen atom is replaced.  
 Also for the latter alkyl group, the  $C_1$ - $C_6$  alkyl can be substituted with from 1 to 3

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substituents, suitably 1, selected from the group consisting of C<sub>1</sub>-C<sub>4</sub> alkoxy, aryl, heterocyclyl, and C(=Y)R<sup>8</sup> or C(=Y)NR<sup>9</sup>R<sup>10</sup> of (6) for R<sup>5</sup> of Structure III referred to above, oxiranyl and glycidyl; such that no more than two of R<sup>13</sup>, R<sup>14</sup> and R<sup>15</sup> are hydrogen (preferably no more than one of R<sup>13</sup>, R<sup>14</sup> and R<sup>15</sup> is hydrogen). Suitable

5 examples of particularly useful initiators are reported to be: 1-phenylethyl chloride and 1-phenylethyl bromide (e.g., where R<sup>13</sup> = Ph, R<sup>14</sup> = CH<sub>3</sub>, R<sup>15</sup> = H and X = Cl or Br), chloroform, carbon tetrachloride, 2-chloropropionitrile, C<sub>1</sub>-C<sub>6</sub>-alkyl esters of a 2-halo-C<sub>1</sub>-C<sub>6</sub>-carboxylic acid (such as 2-chloropropionic acid, 2-bromopropionic acid, 2-chloroisobutyric acid, 2-bromoisobutyric acid, and the like

10 known to those skilled in the art) and compounds of the formula C<sub>6</sub>H<sub>x</sub>(CH<sub>2</sub>Y')<sub>y</sub>, where Y' is Cl or Br, x + y = 6 and y > 1. More preferred initiators include 1-phenylethyl chloride, 1-phenylethyl bromide, methyl 2-chloropropionate, ethyl 2-chloropropionate, methyl 2-bromopropionate, ethyl 2-bromoisobutyrate, α,α'-dichloroxylene, α,α'-dibromoxylene and hexakis(α-bromomethyl)benzene. Also

15 any other initiators disclosed in WO96/30421 and/or WO97/1824 and/or WO98/01480 can be used.

#### TRANSITION METAL FOR ATRP

Transition metal compounds reported to be useful in ATRP are those which

20 can participate in a redox cycle with the initiator and dormant polymer chain. The transition metals are limited in that they do not readily and preferably don't form a direct carbon-metal bond with the polymer chain under ATRP conditions. The more suitable transition metal compounds are those of the formula M<sub>t</sub><sup>n+</sup>X'<sub>n</sub>, where:

M<sub>t</sub><sup>n+</sup> may be selected from the group consisting of Cu<sup>1+</sup>, Cu<sup>2+</sup>, Fe<sup>2+</sup>, Fe<sup>3+</sup>,

25 Ru<sup>2+</sup>, Ru<sup>3+</sup>, Cr<sup>2+</sup>, Cr<sup>3+</sup>, Mo<sup>0</sup>, Mo<sup>+</sup>, Mo<sup>2+</sup>, Mo<sup>3+</sup>, W<sup>2+</sup>, W<sup>3+</sup>, Rh<sup>3+</sup>, Rh<sup>4+</sup>, Co<sup>+</sup>, Co<sup>2+</sup>, Re<sup>2+</sup>, Re<sup>3+</sup>, Ni<sup>0</sup>, Ni<sup>+</sup>, Mn<sup>3+</sup>, Mn<sup>4+</sup>, V<sup>2+</sup>, V<sup>3+</sup>, Zn<sup>+</sup>, Zn<sup>2+</sup>, Au<sup>+</sup>, Au<sup>2+</sup>, Ag<sup>+</sup> and Ag<sup>2+</sup>.



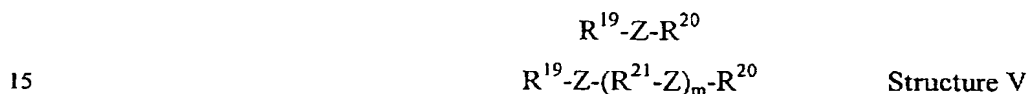
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X' is selected from the group consisting of halogen, C<sub>1</sub>-C<sub>6</sub>-alkoxy, (SO<sub>4</sub>)<sub>1/2</sub>, (PO<sub>4</sub>)<sub>1/3</sub>, (HPO<sub>4</sub>)<sub>1/2</sub>, (H<sub>2</sub>PO<sub>4</sub>), triflate, hexafluorophosphate, methanesulfonate, arylsulfonate (preferably benzenesulfonate or toluenesulfonate), SeR<sup>17</sup>, CN and R<sup>18</sup>CO<sub>2</sub>, where R<sup>17</sup> is as defined above and R<sup>18</sup> is hydrogen or a straight or branched C<sub>1</sub>-C<sub>6</sub> alkyl group (usually methyl) which may be substituted from 1 to 5 times with a halogen (usually 1 to 3 times with fluorine or chlorine); and n is the formal charge on the metal (e.g., 0 < n < 7). Also any other transition metal catalysts disclosed in WO96/30421 and/or WO97/1824 and/or WO98/01480 can be used.

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#### LIGANDS FOR ATRP

Suitable ligands for use in ATRP are reported to be ligands as those mentioned above and more suitably those nitrogen (N-), oxygen (O-), phosphorus (P-) and sulfur (S-) containing ligands which may have one of the following formulas:



In Structure V, R<sup>19</sup> and R<sup>20</sup> can be independently selected from the group consisting of hydrogen, C<sub>1</sub>-C<sub>20</sub> alkyl, aryl, heterocyclyl, and C<sub>1</sub>-C<sub>6</sub> alkyl substituted with C<sub>1</sub>-C<sub>6</sub> alkoxy, C<sub>1</sub>-C<sub>4</sub> dialkylamino, the C(=Y)R<sup>8</sup>, C(=Y)NR<sup>9</sup>R<sup>10</sup>, and YC(=Y)R<sup>11</sup> of (6) for R<sup>4</sup> and R<sup>5</sup> of Structure III. Also R<sup>19</sup> and R<sup>20</sup> can be joined to form a saturated, unsaturated or heterocyclic ring as in a "heterocyclyl" group. Also Z is O, S, NR<sup>22</sup> or PR<sup>22</sup>, where R<sup>22</sup> is selected from the same group as R<sup>19</sup> and R<sup>20</sup>. Also each R<sup>21</sup> is independently a divalent group selected from the group consisting of C<sub>2</sub>-C<sub>4</sub> alkylene (alkanediyl) and C<sub>2</sub>-C<sub>4</sub> alkenylene where the covalent bonds to each Z are at vicinal positions (e.g., in a 1,2-arrangement) or at β-positions (e.g., in a 1,3-arrangement), and from C<sub>3</sub>-C<sub>8</sub> cycloalkanediyl, C<sub>3</sub>-C<sub>8</sub> cycloalkenediyl, arenediyl and heterocyclylene where the covalent bonds to each Z are at vicinal positions. In Structure V, m is from 1 to 6. Suitable ring systems for the present ligand include bipyridine, bipyrrrole, 1,10-phenanthroline, a cryptand, and a crown ether.

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In addition to the above ligands, various ring structures between the groups present in Structure V are possible. For instance, each of  $R^{19}$ -Z and  $R^{20}$ -Z can form a ring with the  $R^{21}$  group to which the Z is bound to form a linked or fused heterocyclic ring system, like a "heterocyclyl" group. Alternatively, Z can be a covalent bond  
5 (which may be single or double),  $CH_2$  or a 4- to 7-membered ring fused to  $R^{19}$  and/or  $R^{20}$ , in addition to the definitions given above for Z, when  $R^{19}$  and/or  $R^{20}$  are heterocyclyl. Where Z is  $PR^{22}$ ,  $R^{22}$  can also be  $C_1$ - $C_{20}$ -alkoxy.

Several other types of suitable ligands reported useful in ATRP processes include CO (carbon monoxide), porphyrins and porphycenes,  $C_1$ - $C_6$  alkyl groups,  $C_1$ -  
10  $C_6$ -alkoxy groups,  $C_1$ - $C_6$  alkoxycarbonyl, aryl groups, heterocyclyl groups, and  $C_1$ - $C_6$  alkyl groups further substituted with from 1 to 3 halogens. The porphyrins and porphycenes can be substituted with from 1 to 6, preferably from 1 to 4, halogen atoms. Other suitable types include compounds of the formula  $R^{23}R^{24}C(C(=Y)R^8)_2$ , where Y and  $R^8$  are as defined above. Each of  $R^{23}$  and  $R^{24}$  are independently selected  
15 from the group consisting of hydrogen, halogen,  $C_1$ - $C_{20}$  alkyl, aryl and heterocyclyl, and  $R^{23}$  and  $R^{24}$  may be joined to form a  $C_3$ - $C_8$  cycloalkyl ring or a hydrogenated (i.e., reduced, non-aromatic or partially or fully saturated) aromatic or heterocyclic ring. Additionally, any of these (except for hydrogen and halogen) may be further substituted with 1 to 5, and preferably 1 to 3,  $C_1$ - $C_6$  alkyl groups,  $C_1$ - $C_6$  alkoxy  
20 groups, halogen atoms and/or aryl groups. One of  $R^{23}$  and  $R^{24}$  can have hydrogen or a negative charge.

Also ethylenediamine and propylenediamine are suitable ligands by themselves or where both of which may be substituted from one to four times on the amino nitrogen atom. The substitution may be with a  $C_1$ - $C_4$  alkyl group or a  
25 carboxymethyl group, aminoethanol, and aminopropanol, any of which may be substituted from one to three times on the oxygen and/or nitrogen atom with a  $C_1$ - $C_4$  alkyl group. Other ligands include ethylene glycol and propylene glycol, both of

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which may be substituted one or two times on the oxygen atoms with a C<sub>1</sub>-C<sub>4</sub> alkyl group; diglyme; triglyme; or tetraglyme.

Suitable carbon-based ligands are reported to include arenes and the cyclopentadienyl ligand. Also carbon-based ligands include benzene (which may be substituted with from one to six C<sub>1</sub>-C<sub>4</sub> alkyl groups such as methyl and cyclopentadienyl). The latter may be substituted with from one to five methyl groups, or may be linked through an ethylene or propylene chain to a second cyclopentadienyl ligand. Where the cyclopentadienyl ligand is used, it is reported that it may not be necessary to include a counteranion (X<sup>-</sup>) in the transition metal compound. All the additional examples of ligands included in the aforementioned world patent documents can also be used including crown ethers such as 18-crown-6. The most preferred ligands are bipyridine and (R<sup>16</sup>O)<sub>3</sub>P. Also any other ligands disclosed in WO96/30421 and/or WO97/1824 and/or WO98/01480 can be used.

The more suitable ligands are unsubstituted and substituted pyridines and bipyridines, where the substituted pyridines and bipyridines are heterocyclyl, acetonitrile, 1,10-phenanthroline, porphyrin, cryptands, and crown ethers, bipyridyl, and 4,4'-dialkylbipyridyls.

Several other materials have utility in the ATRP polymerization process as described in the aforementioned PCT published patent applications. These are solubilized catalysts and redox conjugates of the transition metal compound and macroinitiators for conducting radical living polymerization from living carbocationic polymerization. Additionally, conventional polymerizable monomers can be useful along with the ATRP polymerizable monomers to produce a copolymer with an ATRP formed portion and a non-ATRP polymerized portion.

A solubilized catalyst can be used in a manner that results in a homogeneous polymerization system. As noted in the world patent documents, such a method employs a ligand having substituents rendering the transition metal-ligand complex at least partially soluble, preferably more soluble than the corresponding complex in

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which the ligand does not contain the substituents, and more preferably, at least 90 to 99% soluble in the reaction medium. Examples of suitable ligands are described in WO97/18247 (publication number). Therein the particularly preferred ligands for homogeneous ATRP include: 2,2'-bipyridyl having at least two alkyl substituents  
5 containing a total of at least eight carbon atoms, such as 4,4'-di-(5-nonyl)-2,2'-bipyridyl (dNbipy), 4,4'-di-n-heptyl-2,2'-bipyridyl (dNbipy) and 4,4'-di-tert-butyl-2,2'-bipyridyl (dTbipy).

#### DEACTIVATOR FOR ATRP

10 Also as noted in the WO97/18247 (publication number), ATRP can be conducted wherein a proportion (e.g., 0.1-99.9 mol%, preferably 0.2-10 mol% and more preferably 0.5-5 mol%) of the transition metal catalyst is in an oxidized or reduced state, relative to the bulk of the transition metal catalyst. The oxidized or reduced transition metal catalyst is the redox conjugate of the primary transition metal  
15 catalyst; For example for the  $M_l^{n+}:M_l^{m+}$  redox cycle, 90-99.9 mol% of transition metal  $M_l$  atoms may be in the  $n^+$  oxidation state and 0.1-10 mol% of transition metal  $M_l$  atoms may be in the  $m^+$  oxidation state. The term "redox conjugate" refers to the corresponding oxidized or reduced form of the transition metal catalyst. Oxidation states  $n$  and  $m$  are attained by transition metal  $M_l$  as a consequence of conducting  
20 ATRP. The amount of redox conjugate sufficient to deactivate at least some of the radicals which may form at the beginning of polymerization (e.g., the product of self-initiation or of addition of an initiator radical or growing polymer chain radical to a monomer) is reported to greatly improve the polydispersity and control of the molecular weight of the product. The effects and importance of rates of exchange  
25 between growing species of different reactivities and different lifetimes, relative to the rate of propagation, was reported to have a tremendous effect on polydispersity and control of molecular weight in living/controlled polymerizations. For example the addition of 1% Cu(II) (redox conjugate) was shown to improve the polydispersity of

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the obtained (co)polymer products. As the amount redox conjugate is increased to a presence of more than 10 mol%, there is no reported adverse effect on polymerization by ATRP, but the polymerization rate may slow to a small extent.

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### MACROINITIATOR

A macroinitiator pursuant to PCT published patent application WO98/01480 can also be present. This enables the synthesis of a block copolymer by combining a "living" carbocationic polymerization with a "living" radical polymerization. Any living cationic polymerization known to those skilled in the art can be used such as that described by Matyjaszewski (Cationic Polymerizations, Mechanism, Synthesis and Applications; Marcel Dekker, Inc., New York, 1996). The macroinitiator is formed by conducting a living carbocationic polymerization or oligomerization (small number of repeating units or mers) where the terminal group is a halogen group. This macroinitiator can be used in the ATRP polymerization. For example, poly(styrene-b-styrene), poly(styrene-b-methylacrylate) and poly(styrene-b-methylmethacrylate) copolymers can be polymerized in this manner. The macroinitiator as described in WO98/01480 can be used as the initiator of the initiating system to polymerize a vinyl monomer in the presence the transition metal compound, and a ligand to form a block copolymer by the ATRP process. Suitable macroinitiators are macromonomers containing at least one functionality such as (but not limited to) hydroxyl, carboxyl, vinyl, amine or thiol.

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### AMOUNTS OF MATERIALS FOR ATRP POLYMERIZATION

The amount of the aforementioned materials for ATRP polymerization can vary to a degree with the efficiency of the initiator, which is generally reported to be at least 50%, preferably >80%, more preferably >90%. Generally, the amount of the initiator can be selected such that the initiator concentration is from  $10^{-4}$  Moles ("M") to 1 Mole, preferably  $10^{-3}$ - $10^{-1}$  M. Alternatively, the initiator can be present

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in a molar ratio of from  $10^{-4}$ :1 to  $10^{-1}$ :1, preferably from  $10^{-3}$ :1 to  $5 \times 10^{-2}$ :1, relative to moles of the monomer. The initiator concentration of 0.1-1 M is particularly useful for preparing end-functional polymers. The molar proportion of transition metal compound relative to initiator is generally that which is effective to polymerize the selected monomer(s). A particularly suitable amount is reported to be from 0.0001:1 to 10:1, preferably from 0.1:1 to 5:1, more preferably from 0.3:1 to 2:1, and most preferably from 0.9:1 to 1.1:1. A reduction in the concentration of transition metal and ligand such as to 0.001:1 may be possible when conducting the polymerization in a homogeneous system. The amount of the ligand is noted as dependent on the number of coordination sites on the transition metal compound which the selected ligand will occupy. Generally, a molar proportion relative to the molar amount of the transition metal compound is that which is effective to polymerize the selected monomer(s). The number of coordination sites on a given transition metal compound which a chosen ligand will occupy is readily understood by those skilled in the art. A useful ratio for the amount of ligand is reported to be selected such that the ratio of (a) coordination sites on the transition metal compound to (b) coordination sites which the ligand will occupy is from 0.1:1 to 100:1, preferably from 0.2:1 to 10:1, more preferably from 0.5:1 to 3:1, and most preferably from 0.8:1 to 2:1. However, as is also known in the art, it is possible for a solvent or for a monomer to act as a ligand. Because of such a possibility, a monomer generally is treated as being (a) distinct from and (b) not included within the scope of the ligand.

Of course, the amounts of more than one type of monomer can vary depending on the type of copolymer to be produced. For random copolymers the amount of one particular monomer may be larger than another type for a copolymer to have a predominant percentage of the polymerization reaction product of this type of monomer. For block copolymers the amounts of the different monomers is as broad as the desired amounts of the different types of blocks in the copolymer. Also

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the order of addition of the different types will be affected by the desired structure or architecture or topology of the desired copolymer. This is particularly the case for structures like comb, star, multilegged copolymers and the like. The amounts and order of addition of the different types of polymers is readily comprehended by those skilled in the art of producing such polymer structures such as in other living polymerization processes. Also instead of or in addition to the separate transition metal compound and the ligand compound, a preformed transition metal and ligand complex can be used.

Additionally, as noted in WO96/30421, and/or WO97/1824 and /or WO98/01480, the polymerization may be assisted by matching of either or both of: (1) the reactivity of the groups in the initiator ( $R^{13}$ ,  $R^{14}$  and  $R^{15}$ ) with the group(s) on the monomer ( $R^4$ - $R^7$ ), and (2) the energetics of bond breaking and bond forming in dormant species (e.g., dormant polymer chains) and transition metal species. Such matching can be conducted as known to those skilled in the art of ATRP polymerization as noted in the world patent documents and appears to depend to some degree on the radical stabilizing effects of the substituents. Also the selection of the monomer, initiator, transition metal compound and ligand should be such that the rate of initiation is not less than 1,000 times. Preferably, this rate is not less than 100 times slower than the rate of propagation and/or transfer of the X group to the polymer radical. The term "propagation" refers to the reaction of a polymer radical with a monomer to form a polymer-monomer adduct radical.

Although not essential to the polymerization, observing certain concentration ranges can limit some disadvantageous effects. These include:

- a) the concentration of growing radicals should not exceeds  $10^{-5}$  mol/L, or there may be too many active species in the reaction;
- b) the concentration of growing radicals should not be is less than  $10^{-9}$  mol/L, or the rate may be undesirably slow;

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- c) the concentration of dormant chains should be less than  $10^{-4}$  mol/L, or the molecular weight of the product polymer may increase dramatically;
- d) concentration of dormant species should not be greater than 3 mol/L, unless the desired molecular weight of the product is small or more oligomeric than polymeric.

#### POLYMERIZATION CONDITIONS FOR ATRP

The ATRP polymerization also can be conducted in accordance with known suspension, emulsion and precipitation polymerization processes in the presence or absence of a solvent. When the polymerization is other than bulk polymerization, solvents that are suitable for use include: ethers, cyclic ethers like tetrahydrofuran and dioxane,  $C_5$ - $C_{10}$  alkanes,  $C_5$ - $C_8$  cycloalkanes which may be substituted with from 1 to 3  $C_1$ - $C_4$  alkyl groups, aromatic hydrocarbon solvents, halogenated hydrocarbon solvents, acetonitrile, dimethylformamide, mixtures of such solvents, and supercritical solvents (such as  $CO_2$ ,  $C_1$ - $C_4$  alkanes in which any hydrogen may be replaced with fluorine). Generally, the solvents that are suitable for the preparation of the (co)polymer: have low chain transfer constant; have the ability to dissolve the initiating system; and do not form a complex with the initiating system. Further non-exclusive examples of such solvents are: diphenylether, diaryl ether, dimethoxybenzene, propylene carbonate, and ethylene carbonate. The low chain transfer constant is as defined in: Polymer Handbook, third edition, J. Brandrup and E.H. Immergut, Editors, II/81. Further examples are those solvents known to those skilled in the art as shown in the aforementioned incorporated world patent documents.

As noted in WO96/30421, the ATRP (co)polymer is generally prepared by: polymerizing one or more radically polymerizable monomers in the presence of an initiator having a radically transferable atom or group, a transition metal compound and a ligand to form a (co)polymer, the transition metal compound being



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capable of participating in a redox cycle with the initiator and a dormant polymer chain, and the ligand being any N-, O-, P- or S- containing compound which can coordinate in a bond to the transition metal or any carbon-containing compound which can coordinate in a bond to the transition metal, such that direct bonds between the transition metal and growing polymer radicals are not formed, and isolating the formed (co)polymer.

Additionally, the process can include:

- (1) polymerizing in the presence of an amount of the corresponding reduced or oxidized transition metal compound which deactivates at least some free radicals;
- (2) an ATRP process in which the improvement comprises polymerizing in a homogeneous system or in the presence of a solubilized initiating/catalytic system;
- (3) an ATRP process using water as a medium.

Bulk polymerization can be conducted in the gas phase, for example by passing the monomer in the gas phase over a bed of the catalyst which has been previously contacted with the initiator and ligand, in a sealed vessel or in an autoclave. Polymerizing may be conducted at a temperature of from -78° to 200°C, preferably from 0° to 160°C and most preferably from 80° to 140°C. The length of time of the reaction should be sufficient to convert at least 10% (preferably at least 50%, more preferably at least 75% and most preferably at least 90%) of the monomer to polymer. Reaction time can vary from several minutes to 5 days, preferably from 30 minutes to 3 days, and most preferably from 1 to 24 hours. The pressure of the polymerization may be from 0.1 to 100 atmospheres, preferably from 1 to 50 atmospheres and most preferably from 1 to 10 atmospheres.

Additionally, the process of polymerization can be a "reverse" ATRP as discussed in the aforementioned WO96/30421 and/or WO97/1824 and /or WO98/01480. In this process the transition metal compound is in its oxidized state,

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and the polymerization is initiated by, for example, a radical initiator such as azobis(isobutyronitrile) ("AIBN"), a peroxide such as benzoyl peroxide (BPO) or a peroxy acid such as peroxyacetic acid or peroxybenzoic acid. The radical initiator is believed to initiate "reverse" ATRP as discussed in the aforementioned world  
5 patent documents.

Polymerization by ATRP may also be conducted in an aqueous medium to prepare water-soluble or water-miscible polymers as disclosed in WO97/1824. An "aqueous medium" refers to a water containing mixture which is liquid at reaction and processing temperatures. Examples include water, either alone or admixed with a  
10 water-soluble liquid such as C<sub>1</sub>-C<sub>4</sub> alcohol, ethylene glycol, glycerol, acetone, methyl ethyl ketone, dimethylformamide, dimethylsulfoxide, dimethylsulfone, hexamethylphosphoric triamide, or a mixture thereof. Additionally, the pH of the aqueous medium may be adjusted to a desired value with a suitable mineral acid or base (e.g., phosphoric acid, hydrochloric acid, ammonium hydroxide, NaOH,  
15 NaHCO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>). However, the preferred aqueous medium is water. The present invention also encompasses the production of water swellable polymers and hydrogels. Hydrogels are polymers which, in the presence of water, do not dissolve, but absorb water and thus swell in size.

## 20 (CO)POLYMER MATERIAL

Generally, the ATRP "(co)polymers" can be any of those produced as disclosed in WO96/30421, and/or WO97/1824, and/or WO98/01480. For instance, the (co)polymers (and/or a block thereof) may have an average degree of polymerization (DP) of at least 2, although the DP can exceed 10, and may have a  
25 weight and/or number average molecular weight of at least 100 g/mol, but can exceed even 3000 g/mol. The present (co)polymers, due to their "living" character, can have a maximum molecular weight without limit. However, from a practical perspective, the present (co)polymers and blocks thereof may have an upper weight or number

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average molecular weight of, e.g., 5,000,000 g/mol, preferably 1,000,000 g/mol, more preferably 500,000 g/mol, and even more preferably less than 100,000 g/mol. For example, when produced in bulk, the number average molecular weight may be up to 1,000,000.

- 5       The number average molecular weight may be determined by size exclusion chromatography (SEC) such as gel permeation chromatography using polystyrene standards or, when the initiator has a group which can be easily distinguished from the monomer(s), by NMR spectroscopy or any other method known to those skilled in the art. The type of ATRP (co)polymer produced can be any type as disclosed in
- 10   WO96/30421 and/or WO97/1824 and/or WO98/01480 such as homopolymers including telechelic and hyperbranched, copolymers such as block, comb, multi-block, star, gradient, random, graft and hyperbranched copolymers.

#### REMOVAL OF HALOGEN

- 15       The foregoing has described the ATRP reaction conditions and materials. With the necessary ATRP materials and conditions available after the desired degree of polymerization is achieved, the addition and elimination reaction for the removal of halogen from the polymer can be conducted before isolation of the polymer. This removal of the halogen is at comparatively mild conditions compared to some
- 20   general halogen replacement reactions that replace the halogen with another inorganic group or moiety. Such a replacing inorganic group need not be completely inorganic in that some carbon can be present but carbon to carbon bonds in such groups are usually absent. With the addition and elimination reaction with the limited polymerizable carbon double bond containing compound (hereinafter
- 25   "LPDB compound"), the group that is added to the polymer results in at least one additional carbon to carbon bond near the terminal or end group or groups of the (co)polymer.

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The meaning of terminal or end group is not limited to just the ends of the main chain of the polymer but includes any side chains as, for example in comb, star, or multi-legged or multi-armed copolymer structures.

Also the meaning of "limited polymerizable" under ATRP conditions is that  
5 at least one set of conditions for conducting ATRP polymerization with the compound would not result in the formation of any more than a couple repeating units (oligomer) of the compound (most preferably none). This is at least one set of limited polymerizing ATRP conditions can be used for that specific monomeric or oligomeric LPDB compound. Hence, the meaning of limited polymerizable does  
10 not require that such a LPDB compound is nonpolymerizable under all ATRP conditions. The ATRP reaction system is that which is necessary to effect the addition reaction between the LPDB compound and the ATRP (co)polymer with the halogen containing group or moiety. It is believed without limiting the invention that with the addition of the LPDB compound to the reaction system of ATRP with  
15 the halogen-containing ATRP (co)polymer, that an addition reaction occurs for adding a carbon to carbon bond where the carbon to halogen bond of the (co)polymer was broken. Additionally, the eliminated halogen like chlorine, bromine, or iodine forms a bond elsewhere than with or on the (co)polymer. Since these LPDB compounds undergo minimal, if any, homopolymerization under the  
20 ATRP reaction conditions, the interaction with the halogen results in the additional bond of carbon to carbon to bond the LPDB compound to the ends or terminal portions of the (co)polymer where the halogen was bound. It is believed without limiting the invention that this addition reaction can occur by an ATRP process where the halogen interacts with the transition metal as in Scheme 1 above to  
25 associate the LPDB compound with the (co)polymer. Also with the availability of the abstractable hydrogen from the LPDB compound and with the elimination of the halogen, the double bond of the added LPDB compound can be reformed.

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With the addition of the LPDB compound to the ATRP polymerization system, the reaction conditions can be those used to conduct the ATRP polymerization. Such suitable conditions can include a temperature of from about - 78° to about 200°C, which can be held for a length of time for reaction sufficient to  
5 dehalogenate at least around 10% of the halogen of the (co)polymer up to substantially dehalogenating the (co)polymer (with less than 10 percent of the available halogen remaining) with the limited polymerizable double bond containing compound, and at a pressure for the addition and elimination reaction of from about 0.1 to about 100 atmospheres. This is even though the LPDB compound does not  
10 polymerize to any great extent under ATRP conditions. Preferably, these reaction conditions include a temperature in the range of 0°C or ambient to 160°C and at ambient pressure, usually not more than 50 atmospheres, for a period of time from less than one hour to more than one hour but usually around one hour and generally not more than around 24 hours. The LPDB compound can be added in an amount  
15 in the range of less than to more than 1 mole per mole of halogen atom in the (co)polymer. The lower amounts would reduce the halogen content of the (co)polymer from ATRP polymerization to a lesser degree than the stoichiometric amount and the excess amounts would favor more complete elimination of the halogen. Although adding large excess amounts of the LPDB compound over the  
20 stoichiometric amount is not preferred. Substantial dehalogenation is possible with an amount of the LPDB compound that approaches the stoichiometric amount or exceeds it.

The LPDB compounds can be those mentioned above for Structure I and preferably are essentially free of and most preferably have no halogen. For  
25 example, R<sub>1</sub> and R<sub>2</sub> can be the same or different alkyl groups like methyl group; phenyl group; alkoxy group; ester group; where at least one of the R<sub>1</sub> and R<sub>2</sub> groups is an organo group while the other can be an organo group or hydrogen. Particularly suitable examples of the LPDB compound include: i) 1,1-

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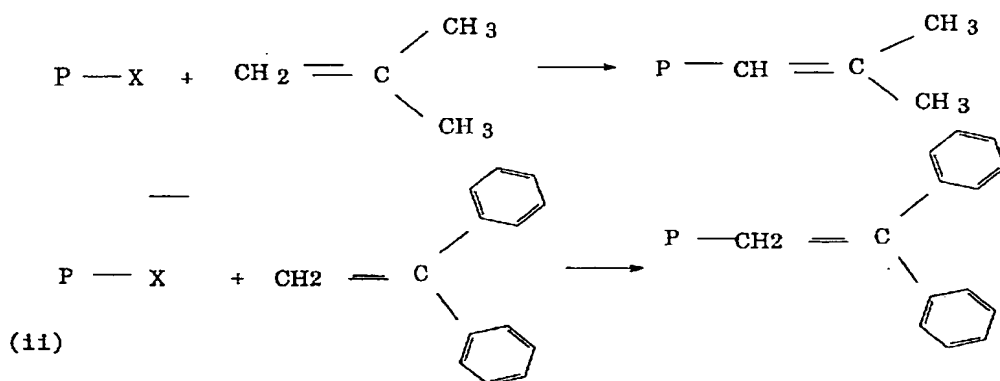
dimethylethylene; ii) 1,1-diphenylethylene; iii) vinyl acetate; iv) isopropenyl acetate; v) alpha-methyl styrene; and vi) 1,1-dialkoxy olefin. Additional examples include dimethyl itaconate and diisobutene (2,4,4-trimethyl-1-pentene).

The reaction product from several of these nonexclusive examples of LPDB  
5 compounds are listed in Table 1 below with the appropriate lower case Roman numeral indication.

Any solvent that does not interfere with the addition and elimination  
reactions can be used. Suitable examples include: ester solvents such as butyl  
acetate, alcohols such as isopropyl alcohol, hydrocarbon solvents such as toluene  
10 and heptane, ketone solvents such as methyl isobutyl ketone and polar solvents such  
as M-Pyrol (N-methyl pyrrolidone), water, and dimethylsulfoxide (DMSO).

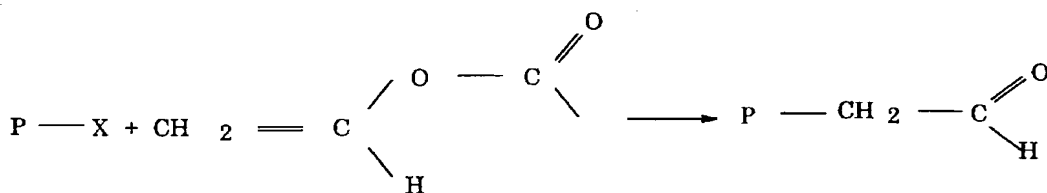
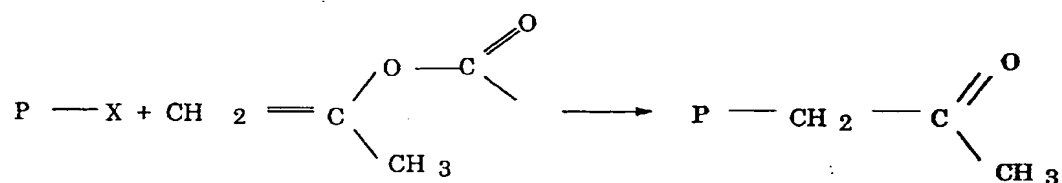
TABLE 1

(i)



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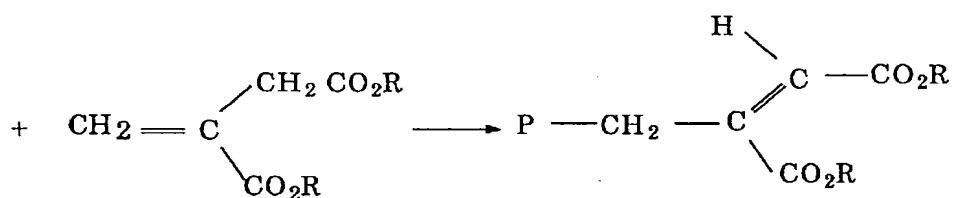
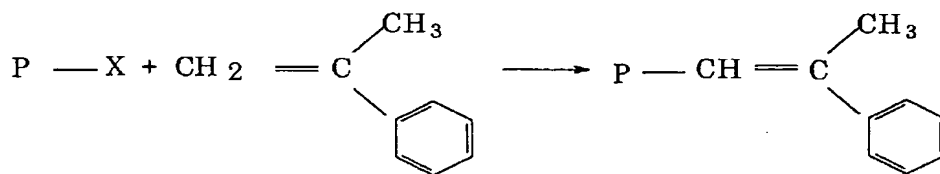
(iii)



(iv)

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(v)



(vi)

10 In the aforementioned structures (i) through (vi), "P" indicates the polymer chain from living polymerization such as ATRP polymerization where the terminal or end group had the halogen. In other words "P" indicates the (co)polymer chain

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portion of an ATRP controlled free radical halogen-containing (co)polymer without the group of the ATRP (co)polymer that contains the halogen.

Also halogen removal from the living (co)polymer can occur after isolation of the (co)polymer where the addition and elimination reactions are conducted in the presence of at least the transition metal and ligand since the initiator halogen  
5 containing group is not necessary. The latter includes the materials such as paratoluenesulfonyl chloride. The reaction conditions would be the same as for the reaction in the presence of the ATRP system.

10

#### SEPARATION OF THE POLYMER

After the polymerizing step is complete, the formed polymer is isolated. The isolating step of the present process is conducted by known procedures, and may comprise evaporating any residual monomer and/or solvent, precipitating in a suitable solvent, filtering or centrifuging the precipitated polymer, washing the polymer and  
15 drying the washed polymer. Transition metal compounds may be removed by passing a mixture containing them through a column or pad of alumina, silica and/or clay. Alternatively, transition metal compounds may be oxidized (if necessary) and retained in the (co)polymer as a stabilizer.

Precipitation can be typically conducted using a suitable C<sub>5</sub>-C<sub>8</sub>-alkane or C<sub>5</sub>-  
20 C<sub>8</sub>-cycloalkane solvent, such as pentane, hexane, heptane, cyclohexane or mineral spirits, or using a C<sub>1</sub>-C<sub>6</sub>-alcohol, such as methanol, ethanol or isopropanol, or any mixture of suitable solvents. Suitable solvents for precipitating are water, hexane, mixtures of hexanes, or methanol. The precipitated (co)polymer can be filtered by gravity or by vacuum filtration, in accordance with known methods (e.g., using a  
25 Buchner funnel and an aspirator). Alternatively, the precipitated (co)polymer can be centrifuged and the supernatant liquid decanted to isolate the (co)polymer. The (co)polymer can then be washed with the solvent used to precipitate the



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polymer, if desired. The steps of precipitating and/or centrifuging, filtering and washing may be repeated, as desired.

Once isolated, the (co)polymer may be dried by drawing air through the (co)polymer, by vacuum, etc., in accordance with known methods (preferably by vacuum). The present (co)polymer may be analyzed and/or characterized by size  
5 exclusion chromatography, NMR spectroscopy, and the like procedures known to those skilled in the art.

### EXAMPLES

10 The following examples illustrate the procedure for conducting ATRP polymerization and removal of the halogen in accordance with the present invention in-situ with the ATRP system where the ATRP polymer was formed.

#### Example 1

15 An amount of 0.005 mole (1.2 g) of  $\text{CuBr}_2$ , 0.01 mole (0.6 g) of Cu powder, 0.02 mole (3.12 g) of 2,2-bipyridyl and 0.02 mole (3.8 g) of p-toluenesulfonyl chloride was added to a mixture of methyl methacrylate ( 6.4 ml) and toluene (4 ml) and the reaction mixture was heated to 80°C. Complete conversion of methyl methacrylate to a polymeric reaction product occurred after 3 hours. An amount of  
20 0.06 mole of alpha-methyl styrene was combined with the unseparated polymeric reaction product and the reaction mixture was heated to 110°C for 1 hour. The resulting polymer was analyzed by Gel Permeation chromatography, and had a Molecular weight, ( $M_n$ ) of 450 and polydispersity ( $M_w/M_n$ ) 1.28 relative to polymethyl methacrylate standards. The composition of the material was determined  
25 by NMR, and GC/MS. The NMR spectrum showed the aromatic peaks from addition of alpha methyl styrene, and subsequent dehydrohalogenation to a C-C double bond at the chain end. GC/MS gave a molecular ion peak which confirmed this structure.

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### Example 2

As in Example 1, a polymeric reaction product was prepared and an amount of 0.06 mole of isopropenyl acetate was combined with the unseparated polymeric reaction product, and the reaction mixture was heated to 110°C for 1 hour. The resulting polymer was analyzed by Gel Permeation chromatography and had a Molecular weight (Mn) of 430 and polydispersity (Mw/Mn) 1.27 relative to polymethyl methacrylate standards. The composition of the material was determined by NMR and GC/MS. The NMR spectrum showed the peaks from addition of isopropenyl acetate, and subsequent dehydrohalogenation to a C=O bond at the chain end. GC/MS gave a molecular ion peak which confirmed this structure.

### Example 3

As in Example 1, a polymeric reaction product was prepared and an amount of 0.06 mole of dimethyl itaconate was combined with the unseparated polymeric reaction product and the reaction mixture was heated to 110°C for 1 hour. The resulting polymer was analyzed by Gel Permeation Chromatography and had a Molecular weight (Mn) of 470 and polydispersity (Mw/Mn) 1.21 relative to polymethyl methacrylate standards. The composition of the material was determined by NMR and GC/MS. The NMR spectrum showed the peaks from the addition of dimethyl itaconate, and subsequent dehydrohalogenation to a C-C double bond at the chain end. GC/MS gave a molecular ion peak which confirmed this structure.

### Example 4

As in Example 1, a polymeric reaction product was prepared and an amount of 0.06 mole of diisobutene (2,4,4-trimethyl-1-pentene) was combined with the unseparated polymeric reaction product, and the reaction mixture was heated to 110°C for 1 hour. The resulting polymer was analyzed by Gel Permeation Chromatography, and had a Molecular weight (Mn) of 490 and polydispersity (Mw/Mn) 1.23 relative to

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polymethyl methacrylate standards. The composition of the material was determined by NMR and GC/MS. The NMR spectrum showed the peaks from addition of diisobutene, and subsequent dehydrohalogenation to a C-C double bond at the chain end. GC/MS gave a molecular ion peak which confirmed this structure.

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We claim:

1. A substantially dehalogenated polymer comprising: the reaction product of (A) a (co)polymer derived from the controlled free radical process where  
5 the (co)polymer has halogen on at least one terminal or end location of the (co)polymer chain from the (co)polymerization reaction under controlled free radical polymerization process conditions, and (B) at least one limited polymerizable double bond containing compound whereby the dehalogenation is accomplished by the addition of said compound to the (co)polymer through the formation of a carbon to  
10 carbon bond on the (co)polymer and the elimination of the halogen from at least one end of the (co)polymer chain.

2. The (co)polymer of claim 1 wherein the halogen-containing (co)polymer (A) is the (co)polymerization reaction product of the controlled free  
15 radical (co)polymerization of one or more radically polymerizable monomers in the presence of: (i) an initiator having a radically transferable atom or group, (ii) a transition metal compound which participates in a reversible redox cycle with said initiator or a dormant (co)polymer chain end, and (iii) a ligand that is any N-, O-, P- or S- containing compound which can coordinate with the transition metal or any  
20 carbon-containing compound, such that direct bonds between the transition metal and growing (co)polymer radicals are not formed, and wherein the transition metal compound and said ligand provide reaction with the initiator to reversibly generate a radical for polymerization; and wherein the initiator has at least one halogen group that is incorporated into the (co)polymer.

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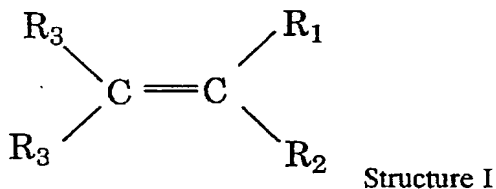
3. The (co)polymer of claim 1 wherein the limited polymerizable double bond containing compound is essentially free of halogen.

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4. The (co)polymer of claim 1 that has less than 100,000 number average molecular weight.

5. The (co)polymer of claim 1 that has less than 10,000 number average molecular weight.

6. The (co)polymer of claim 1 wherein the limited polymerizable double bond containing compound has the structure of:



10 wherein  $R_1$  and  $R_2$  can be the same or different organic groups selected from alkyl groups having a number of carbon atoms from 1 to 4; aryl groups, alkoxy groups; ester groups; alkyl sulfur groups, acyloxy groups, nitrogen-containing alkyl groups where at least one of the  $R_1$  and  $R_2$  groups is an organo group while the other can be an organo group or hydrogen, and wherein the  $R_3$  group is the same or different  
15 group selected from hydrogen, lower alkyl, and organic groups that can be joined to the  $R_1$  or the  $R_2$  groups to form a cyclic compound, and where the  $R_1$ ,  $R_2$  and  $R_3$  groups are selected such that the addition reaction of the halogen-containing (co)polymer to the double bond is not prevented.

20 7. The (co)polymer of claim 6 wherein the limited polymerizable double bond containing compound is selected from the group consisting of: i) 1,1-dimethylethylene; ii) 1,1-diphenylethylene; iii) vinyl acetate; iv) isopropenyl acetate; v) alpha-methyl styrene; vi) 1,1-dialkoxy olefin, vii) dimethyl itaconate, and viii) diisobutene (2,4,4-trimethyl-1-pentene).

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8. The (co)polymer of claim 6 wherein the polymerizable monomer is selected from the group consisting of: methyl acrylate (MA), methyl methacrylate (MMA), butyl acrylate (BA), 2-ethylhexyl acrylate (EHA), acrylonitrile (AN),  
5 styrene and combinations of any two or more of these.

9. The (co)polymer of claim 8 wherein the transition metal compound is selected from the group consisting of: copper chloride and copper bromide and combinations thereof; and wherein the initiator is selected from the group consisting  
10 of: 1-phenylethyl chloride; 1-phenylethyl bromide; methyl 2-chloropropionate; ethyl 2-chloropropionate; methyl 2-bromopropionate; ethyl 2-bromoisobutyrate;  $\alpha,\alpha'$ -dichloroxylylene;  $\alpha,\alpha'$ -dibromoxylylene; and hexakis( $\alpha$ -bromomethyl)benzene; and wherein the ligand is selected from the group consisting of: unsubstituted and substituted pyridines and bipyridines, where the substituted pyridines and bipyridines  
15 are heterocyclyl, acetonitrile, 1,10-phenanthroline, porphyrin, cryptands, and crown ethers, bipyridyl, and 4,4'-dialkylbipyridyls; 2,2'-bipyridyl having at least two alkyl substituents containing a total of at least eight carbon atoms.

10. The (co)polymer of claim 6 wherein compound of Structure I is  
20 added in an amount of around 1 mole per mole of halogen atom in the halogen containing controlled free radical (co)polymer.

11. A (co)polymer with a reduced halogen content produced by controlled free radical polymerization with a halogen-containing material comprising  
25 the reaction product of:

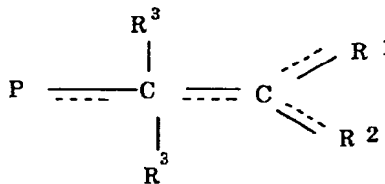
A) a (co)polymer having at least one terminal end group with halogen produced from radically polymerizing one or more radically polymerizable monomers in the presence of: (i) an initiator having a radically transferable atom or group, (ii)

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- transition metal compound which participates in a reversible redox cycle with said initiator or a dormant (co)polymer chain end, and (iii) ligand that is any N-, O-, P- or S- containing compound which can coordinate with the transition metal (ii) or any carbon-containing compound which can coordinate with the transition metal (ii), such
- 5 that direct bonds between the transition metal and growing (co)polymer radicals are limited, and wherein the transition metal compound and said ligand provide reaction with the initiator to reversibly generate a radical for polymerization, and where at least one of (i), (ii), or (iii) are halogen-containing material where the halogen becomes part of the controlled free radical (co)polymer; and
- 10 B) at least one limited polymerizable double bond containing compound that does not polymerize under at least one set of conditions for polymerizing the (co)polymer of (A).

12. A (co)polymer with a reduced halogen content of claim 11 wherein
- 15 the initiator is the halogen-containing material and halogen is the atom or part of the group transferred to the (co)polymer.

13. An ATRP produced living (co)polymer with a reduced halogen content having the structure:



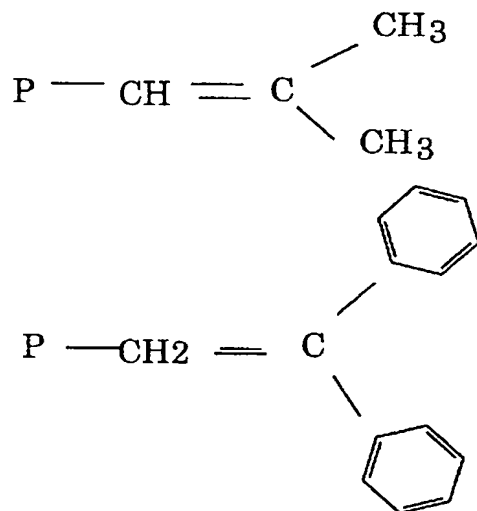
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wherein "P" indicates the (co)polymer chain portion of an ATRP halogen-containing (co)polymer without the group of the ATRP (co)polymer that contains the halogen and wherein  $\text{R}_1$  and  $\text{R}_2$  can be the same or different organic groups

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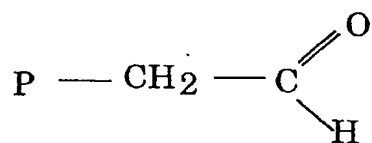
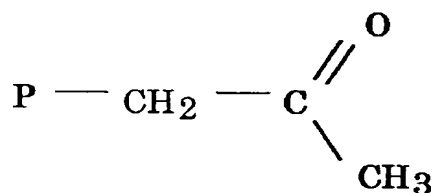
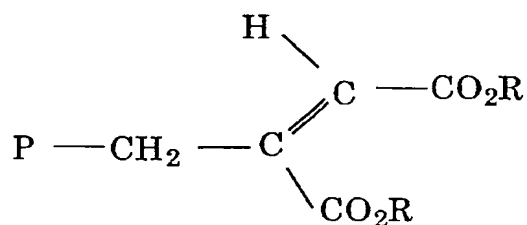
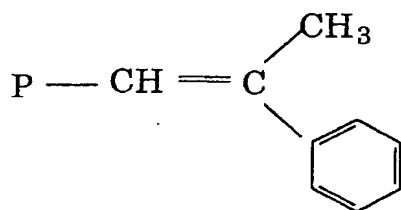
selected from alkyl groups having a number of carbon atoms from 1 to 4; aryl groups, alkoxy groups; ester groups; alkyl sulfur groups, acyloxy groups, nitrogen-containing alkyl groups where at least one of the  $R_1$  and  $R_2$  groups is an organo group while the other can be an organo group or hydrogen, and wherein the  $R_3$  group is the same or different group selected from hydrogen, lower alkyl, and organic groups that can be joined to the  $R_1$  or the  $R_2$  group to form a cyclic compound, and where the  $R_1$ ,  $R_2$ , and  $R_3$  groups are selected such that the addition reaction of the halogen-containing (co)polymer to the double bond is not prevented.

- 10 14. An ATRP produced living (co)polymer with a reduced halogen content having the structure selected from the group consisting of:





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wherein "P" indicates the (co)polymer chain portion of an ATRP controlled free radical halogen-containing (co)polymer without the group of the ATRP (co)polymer that contains the halogen.

15. Method of reducing the halogen content of a halogen-containing (co)polymer produced from controlled polymerization by atom or group transfer radical polymerization where one or more radically (co)polymerizable monomers are radically polymerized in the presence of: (i) an initiator having a radically transferable

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halogen atom or halogen-containing group, (ii) transition metal compound, and (iii) any N-, O-, P- or S- containing ligand, comprising:

5 I) combining with the (co)polymer at least one limited polymerizable double bond containing compound in the presence of the transition metal compound (ii), and the N-, O-, P- or S- containing ligand (iii) whereby dehalogenation is accomplished by the addition of said compound to the (co)polymer through the formation of a carbon to carbon bond on the (co)polymer and elimination of the halogen from at least one end of the (co)polymer chain.

10 16. Method of claim 15, wherein the at least one limited polymerizable double bond containing compound is combined with the halogen-containing (co)polymer in the presence of an initiator having a radically transferable atom or group in addition to the transition metal compound (ii), and the N-, O-, P- or S- containing ligand (iii).

15 17. Method of claim 15, wherein the halogen-containing (co)polymer is produced from controlled polymerization by atom or group transfer radical polymerization where one or more radically (co)polymerizable monomers are radically polymerized in the presence of: (i) an initiator having a radically transferable  
20 halogen atom or halogen-containing group, and a catalyst system comprising (ii) a transition metal compound which participates in a reversible redox cycle with said initiator or a dormant (co)polymer chain end, and (iii) a ligand which is any N-, O-, P- or S- containing compound which can coordinate with the transition metal or any carbon-containing compound which can coordinate in a bond to the transition metal,  
25 such that direct bonds between the transition metal and growing (co)polymer radicals are limited.

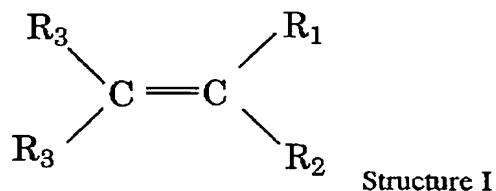
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18. Method of claim 15, which includes separating (co)polymer with the reduced halogen content from the presence of the transition metal compound (ii) and the ligand (iii).

5 19. Method of claim 15, wherein the limited polymerizable double bond containing compound is combined with the halogen-containing (co)polymer at a temperature of from about -78° to about 200°C, and held for a length of time for reaction sufficient to dehalogenate at least 10% of the halogen of the (co)polymer with the limited polymerizable double bond containing compound, and at a pressure  
10 for the addition and elimination reaction of from about 0.1 to about 100 atmospheres.

20. Method of claim 19, wherein the temperature is in the range from 0° to 160°C and the reaction time is in the range of from 1 to 24 hours and the  
15 pressure is in the range of 1 to 50 atmospheres.

21. Method of claim 15, wherein the limited polymerizable double bond containing compound has the structure of:



20 wherein R<sub>1</sub> and R<sub>2</sub> can be the same or different organic groups selected from alkyl groups having a number of carbon atoms from 1 to 4; aryl groups, alkoxy groups; ester groups; alkyl sulfur groups, acyloxy groups, nitrogen-containing alkyl groups where at least one of the R<sub>1</sub> and R<sub>2</sub> groups is an organo group while the other can be an organo group or hydrogen, and wherein the R<sub>3</sub> group is the same or different  
25 group selected from hydrogen, lower alkyl groups, and organic groups that can be

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joined to the  $R_1$  or the  $R_2$  group to form a cyclic compound, and where the  $R_1$ ,  $R_2$ , and  $R_3$  groups are selected such that the addition reaction of the halogen-containing (co)polymer to the double bond is not prevented.

- 5           22.     Method of claim 21, wherein the compound of Structure I is selected from the group consisting of: i) 1,1-dimethylethylene; ii) 1,1-diphenylethylene; iii) vinyl acetate; iv) isopropenyl acetate; v) alpha-methyl styrene; and vi) 1,1-dialkoxy olefin.

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 99/08191

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08F8/26

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 98 01480 A (CARNEGIE-MELLON UNIVERSITY) 15 January 1998 (1998-01-15) cited in the application claims 1-39	1-22
Y	EP 0 789 036 A (KANEKA CORPORATION) 13 August 1997 (1997-08-13) page 4, line 10 - line 51 page 5, line 22 - line 54 page 9, line 2 - line 31; claims 1-25	1-22
A	EP 0 101 541 A (DYNAMIT NOBEL AG) 29 February 1984 (1984-02-29) page 7, line 32 - page 10, line 12; claims 1-5	1
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents :

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Date of the actual completion of the international search

29 July 1999

Date of mailing of the international search report

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# INTERNATIONAL SEARCH REPORT

Int. Jona! Application No  
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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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